Polarization Propagator for X-Ray Spectra

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A polarization propagator for x-ray spectra is outlined and implemented in density functional theory. It rests on a formulation of a resonant-convergent first-order polarization propagator approach which makes it possible to directly calculate the x-ray absorption cross section at a particular frequency without explicitly addressing the excited states. The quality of the predicted x-ray spectrum relates only to the type of density functional applied without any separate treatment of dynamical relaxation effects.

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Introduction.—X-ray spectroscopy, the oldest tool in natural sciences to investigate the elementary composition, electronic, and geometric structure of matter, has experienced a great revival in recent years much owing to the development of synchrotron radiation facilities. This revival is now further spurred by the envisioning of the forthcoming 4th generation radiation sources with ultrashort, femtosecond, pulses with space and time coherence that will open a broad avenue of scientific issues of fundamental and applied character, with emerging new disciplines such as x-ray femtochemistry, dynamic x-ray Raman spectroscopy, and femtoscale diffractional scattering, and that will help to solve essential problems in materials and life sciences [1]. The completion of—still in some years to come—x-ray free-electron lasers with outstanding performance can produce a paradigm shift in natural sciences, for instance, in protein biology with the possibilities to study single proteins and membrane proteins *in situ* or in materials science with the possibility to follow femtosecond dynamics at atomic dimensions.

It stands beyond doubt that a concomitant development in theory and simulation technology is called for. Traditionally, the use of x-ray spectroscopy can be traced to the localized nature of the core electron involved in an x-ray transition, which implies effective selection rules, valuable for mapping the local electron structure, and a chemical shift that carries conformational information. From a theoretical point of view, the core electron localization is a complicating factor that inflicts large relaxation of the valence electron cloud in a semistationary state that is embedded in an electronic continuum. Treatments of relaxation effects have favored the restricted in scope, state-specific methods whereas polarization propagator methods that otherwise form a universal approach to determine spectroscopic properties in the optical and ultraviolet regions have been disfavored. A propagator based formalism has several formal and practical advantages in that it explicitly optimizes the ground-state wave function (or density) only, it ensures orthogonality among states, it preserves gauge operator invariance, sum rules, and general size consistency, and it is applicable to all standard electronic structure methods (wave function and density based). Furthermore, it gives much improved oscillator strengths and other spectroscopically related properties as compared to state-specific methods. It would therefore be highly consequential to extend the applicability of propagator approaches to the family of x-ray spectroscopies.

In the present work, we demonstrate that it is indeed possible to construct an electronic polarization propagator which is applicable not only in the traditional optical region but also in the x-ray region. We overcome the difficulties described above by formulating a resonant-convergent first-order polarization propagator, where absorption is included in the formalism, making it thereby possible to directly calculate the absorption cross section at a particular frequency without explicitly addressing the excited states. We demonstrate that the proposed approach has the same qualities and virtues for x-ray spectroscopies as traditional propagator approaches have long shown for optical spectroscopies. Apart from being a direct, time-dependent approach for calculating the x-ray absorption spectrum, with proper account of relaxation effects, the resonant-convergent polarization propagator method is open-ended towards extensions to properties and spectra in the x-ray region in general, for instance, x-ray dichroic and nonlinear spectroscopies such as multiphoton x-ray absorption that will be experimentally observable with the forthcoming x-ray free-electron lasers [2].

Theory.—The cross section for linear absorption of radiation by a randomly oriented molecular sample can, in the electric-dipole approximation, be expressed as

$$\sigma(\omega) = \frac{4\pi\omega}{c}\mathrm{Im}\bar{\alpha}(\omega), \tag{1}$$

where $\bar{\alpha}$ denotes the trace of the complex electric-dipole polarizability tensor. We note that the real part of α corresponds to the refractive index of the sample. By introducing damping terms γ_n that correspond to the inverse lifetimes of the exponentially decaying excited states of the system, a quantum mechanical expression for the molecular polarizability can be written as a sum over the excited states according to

$$\alpha_{\alpha\beta}(\omega) = \hbar^{-1}\sum_{n>0}\left\{\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{0n} - \omega - i\gamma_n} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{0n} + \omega + i\gamma_n}\right\}. \tag{2}$$

In approximate state electronic structure theory, the use of Eq. (2) is very limited. Instead, in time-dependent polarization propagator theory, one traditionally adopts the infinite lifetime approximation ($\gamma_n = 0$) and converts Eq. (2) into a matrix equation in which any explicit reference of the excited states is avoided. The corresponding polarization propagator is real and resonant divergent. Absorption properties are given in terms of the eigenvectors of the electronic Hessian that are found by a bottom-up approach, which means that one can address only the first few valence excited states. One pragmatic way to address high-lying excitations, such as core electron excitations, is to construct a limited Hessian based on a restricted set of electron excitation operators (the restricted channel approach). However, such an approach will not be able to account for the electronic relaxation of the core-hole state and will thus be quite inaccurate, in general.

In the present work, we demonstrate that a recent extension of propagator methods that implements Eq. (2) inherently provides the possibility to address the relaxation effects in x-ray spectroscopies while maintaining other favorable features of propagator theory. In this *complex polarization propagator* (CPP) approach [3], the polarizability is given by the solution to the response equation

$$\alpha_{\alpha\beta} = -\mu_\alpha^{[1]\dagger}[E^{[2]} - (\omega + i\gamma)S^{[2]}]^{-1}\mu_\beta^{[1]}, \tag{3}$$

where $\mu_\alpha^{[1]}$ is the electric-dipole property gradient along the molecular axis α, $E^{[2]}$ is the electronic Hessian, and $S^{[2]}$ is a metric (overlap matrix). Using this approach, the absorption at a particular frequency can be computed at a constant computational cost and memory usage, no matter how many states are involved and without having to determine the eigenvectors of the electronic Hessian. In this way, the energy region of interest can be sampled with an energy spacing corresponding to the linewidths (a common linewidth $\gamma_n = \gamma$ is used in the present work). Since we make no approximations in the propagator (for a given electronic structure method), our approach has the potential to be exact for the electronic absorption. We stress that explicit reference of the excited states is not made.

Calculations.—To show the qualities of the CPP approach, we have calculated the near-edge x-ray absorption fine structure (NEXAFS) spectra of the oxygen K edge in water and the carbon, nitrogen, and oxygen K edge in the guanine-cytosine and adenine-thymine base pairs; see Fig. 1 for molecular structures. The calculations have been performed with a locally modified version of the DALTON program [4] at the Kohn-Sham density functional theory (DFT) level using the van Leeuwen–Baerends 1994 (LB94) [5] and the hybrid Becke three-parameter exchange–Lee-Yang-Parr correlation functional using the Coulomb-attenuating method (CAM-B3LYP) [6] exchange-correlation functionals. The latter functional is to a varying degree including long-range Coulomb interactions (indicated in parenthesis below). For comparison with previous theoretical work, we have also calculated the spectrum for water using the state-specific static exchange (STEX) method. We have employed basis sets of double-ζ quality: taug-cc-pVDZ [7] for water and 6-31G [8] for the base pairs.

In the case of water (Fig. 2), excellent absorption spectra are obtained with the LB94 and CAM-B3LYP (100%) functionals. We compare here with the STEX calculation which includes relaxation (albeit not the so-called screening relaxation) but otherwise excludes electron correlation effects. The CPP approach makes no distinction between the two effects and would, in principle, give the correct answer, provided we knew the correct density functional.

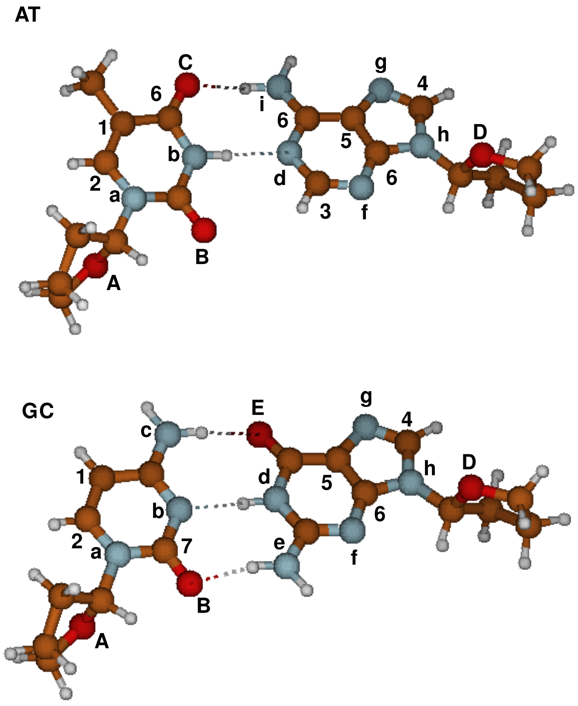

FIG. 1 (color online). Molecular structure of guanine-cytosine.

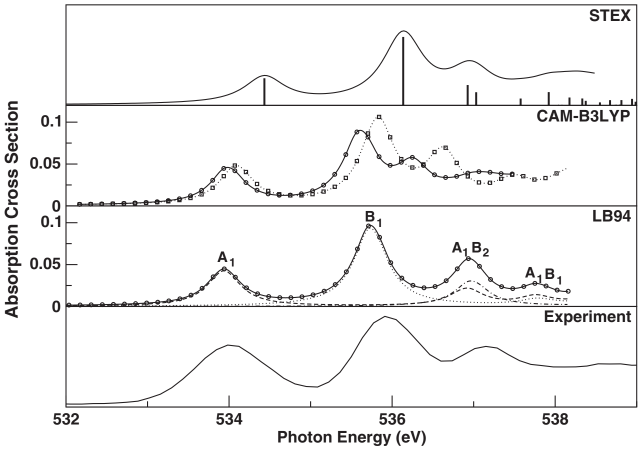

FIG. 2. *K*-edge NEXAFS spectrum of water. The CAM-B3LYP results are obtained with 65% (circles) and 100% (squares) long-range Coulomb interaction. The LB94 results show individual components and averaged value (solid line with circles). The spectra have been shifted by 15.15 (CAM-B3LYP) and 4.0 eV (LB94). The experimental results are taken from Ref. [9].

Both of the functionals tested here give too low excitation energies, a fact that can be directly related to the self-interaction error in the core. However, the effect of this error is only to provide a constant shift of the absorption energies and does not hamper the use of the CPP method for the purpose of spectral analysis. For both LB94 and CAM-B3LYP (100%) functionals, the obtained spectra show a slight "compression" of the absorption below the ionization threshold; for CAM-B3LYP (65%), the compression is larger due to the inexact asymptotic behavior of this functional. We note that a small compression is present also in the STEX spectrum, in this case due to overscreening in the ionic reference state.

The polarization dependency of the absorption is directly given by considering the individual polarizability tensor elements. This can also be used as a basis for symmetry analysis of the participating states as well as to give atomic site structure information. We present the individual components of the linear absorption cross section $\sigma_\alpha(\omega)$ for the case of water in Fig. 2, which thus corresponds to the absorption due to an electric field polarized along the molecular axis α; the total absorption in Eq. (1) is the sum of the three components.

For large-scale, low symmetry applications with a multitude of inequivalent atomic centers, it is important not only to obtain the polarization dependence of the absorption but also to attribute spectral peaks to individual atoms. In a state-specific approach, this would call for an optimization of the excited states with core holes localized to all of the individual atoms, one at a time. This information may at first appear absent in our direct ground-state based approach where no explicit reference is made of the core-hole state. However, the information about the atom specific absorption is contained in the response vectors of the complex response equation [Eq. (3)]. For the analysis of complex spectra with several small chemical shifts, such as those of the base pair spectra, this information is indispensable.

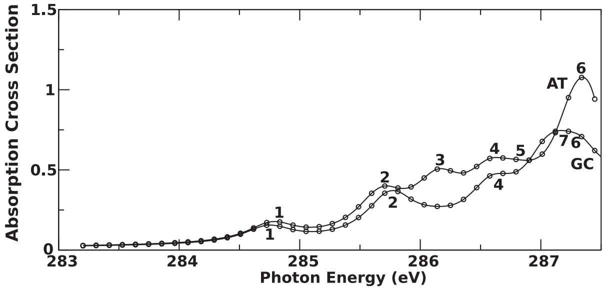

FIG. 3. Carbon *K*-edge NEXAFS spectrum (shifted by 10 eV) of guanine-cytosine and adenine-thymine as determined with the CPP method with DFT and the CAM-B3LYP functional using 100% long-range Coulomb interaction. The absorption peaks are attributed to different atoms according to the labeling in Fig. 1.

The carbon *K*-edge spectra are presented in Fig. 3. At each peak in the spectra, one needs only to identify the dominating element in the imaginary part of the response vector (which corresponds to a specific orbital transfer amplitude) and determine the position of the hole orbital. It is clear that the two base pairs display characteristic differences with respect to the positioning and intensities of some carbons (compare, e.g., peaks attributed to carbons 3, 5, and 7).

In Fig. 4, we show the nitrogen *K*-edge spectra. We illustrate that the division of the total absorption as due to different atoms can be made more detailed by individual plotting of the orbital transfer amplitudes for the entire

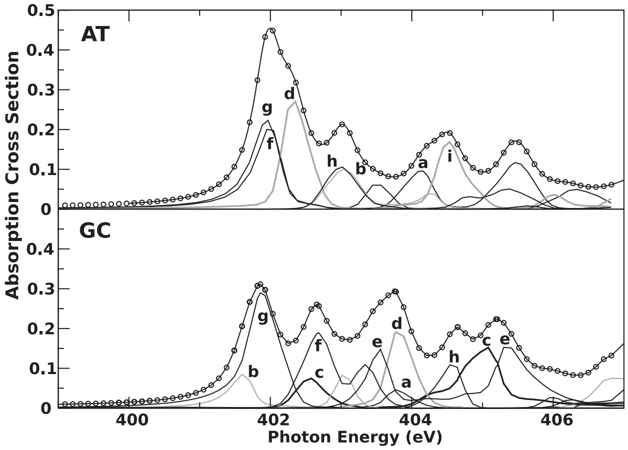

FIG. 4. Nitrogen *K*-edge NEXAFS spectrum (shifted by 14 eV) of guanine-cytosine and adenine-thymine as determined with the CPP method with DFT and the CAM-B3LYP functional using 100% long-range Coulomb interaction. The atom specific absorption (see Fig. 1 for labeling) to the total absorption (resulting solid line) is indicated.

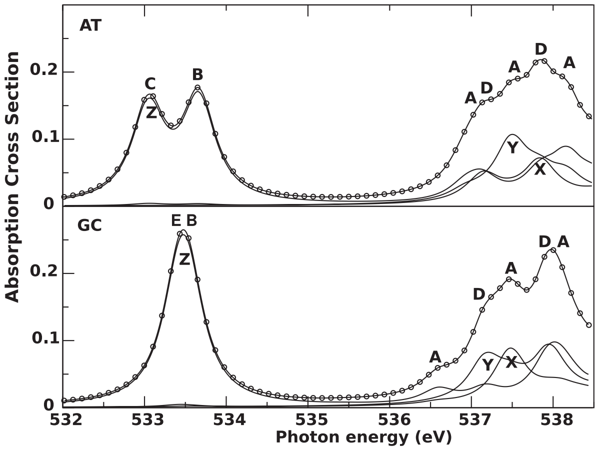

FIG. 5. Oxygen K-edge NEXAFS spectrum (shifted by 15 eV) of guanine-cytosine and adenine-thymine as determined with the CPP method with DFT and the CAM-B3LYP functional using 100% long-range Coulomb interaction. The absorption peaks are attributed to different atoms according to the labeling in Fig. 1, and the absorption contributions for different light polarization is indicated.

range of frequencies. Again, we stress that it is the information contained in a single calculation and *not* several atom specific calculations that is shown.

Finally, we present the oxygen K-edge spectra in Fig. 5. In this figure, we wish to illustrate the information that is contained in the consideration of the three components of the absorption, i.e., the polarization dependence. It is clear that the absorption intensity connected with an electric field polarization perpendicular to the pyrimidine ring is localized to oxygens B, C, and E. The peaks of atoms B and E in the guanine-cytosine base pair overlap as they are both involved in hydrogen bonding, whereas peaks attributed to atoms B and C in the adenine-thymine base pair are separated as only one is involved in hydrogen bonding.

Concluding remarks.—A formulation of an electronic polarization propagator method that is applicable to x-ray spectroscopies has been presented. It represents an electron correlated treatment including relaxation effects of the full x-ray absorption spectrum and solves thereby a long time mismatch in the level of treatment between optical and x-ray spectra. In fact, it makes no distinction of correlation and relaxation effects, with the quality of the computed spectra associating only to the quality of the applied density functional. Apart from the several formal advantages of propagator approaches compared to state-specific approaches, there are practical benefits that can significantly widen the scope of theoretical modeling of x-ray spectroscopies. The kernel in the complex polarization propagator method, formulated as a linear response equation, is solved in the same manner as in traditional time-dependent Kohn-Sham theory with an identical computational scaling. Furthermore, the methodology is open-ended towards extensions to general x-ray properties and spectra, for instance, multiphoton x-ray spectroscopy.

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